Thermochimica Acta 617 (2015) 95–101

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

The influence of CO_2 fixation reaction and nanoclay addition on the curing kinetic parameters of a bifunctioal epoxy resin

Morteza Khoshkish, Mehdy Vafayan*, Hosein Bouhendi

Iran Polymer & Petrochemical Institute, P.O. Box 14965/115, Tehran, Iran

ARTICLE INFO

Article history:
Received 27 June 2015
Received in revised form 19 August 2015
Accepted 21 August 2015
Available online 22 August 2015

Keywords:
CO_2 fixation
Kinetic parameters
Nanoclay

ABSTRACT

The reaction of a bifunctional epoxy resin with carbon dioxide (CO_2) in the presence of tetra-*n*-butyl ammonium bromide was investigated by the FTIR analysis. Unmodified epoxy (UME) and CO_2 fixation modified epoxy (CFME) resins were modified using a nanoclay additive to prepare, respectively, nanoclay modified (NME) and CO_2 fixation/nanoclay modified epoxy (CFNME) resins. The cure kinetic parameters of the resins were calculated by Sbirrazzuoli approach using dynamic DSC data. In this approach the kinetic parameters of Kamal's model and a diffusion model are estimated using the dependency of activation energy on the extent of conversion obtained by an advanced integral isoconversional method. A great change observed in the cure kinetic parameters of CO_2 fixation epoxy resin could be attributed to the formation of 1,3-dioxolane-2-one rings which also showed a considerable interaction with the quaternary ammonium cation of organic modifier in the nanoclay.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The rising concentration of carbon dioxide, a dangerous greenhouse gas (GHG), in the earth's atmosphere is a matter of concern and there is need to find more new and effective ways to consume this material. The carbonation reaction of epoxy resins is one of the new ways for consuming this hazardous gas and converting it to valuable commercial polymeric products [1]. Reaction of CO_2 with epoxy group leads to an important and attractive chemical group known as cyclic carbonate. Because of high solubility, high boiling and flash point, low toxicity and biodegradability, solvents containing cyclic carbonate group are useful aprotic solvents for paint stripping and cleaning applications [2].

CO_2 fixation reaction has been investigated using various catalysts such as alkali ammonium halides [3], halide salts [4], iio liquid salts [1,5–7], quaternary phosphonium salts [2,8], transition-metal complexes [9,10] and ion-exchange resins [11].

Epoxy resin is one of the important resins that its combination with various nanoclay additives has been studied by many researchers [12,13]. While there is some work related to epoxies modified by CO_2 fixation reaction [14], only a few works have been published on the modification of epoxy resins using both CO_2 fixation reaction and nanoclay simultaneously. In a recent work [15] CO_2 has been carried out on 4,4′-methylenebis (*N*,*N*-diglycidyl aniline) (TGDDM), a tetrafunctional epoxy resin, and the dynamical mechanical properties, curing behavior and thermal properties of CO_2 fixated epoxy resin produced were investigated. In our previous work [16] the activation energy dependency of a bifunctional epoxy resin modified simultaneously by both CO_2 fixation reaction and nanoadditive was studied.

In spite of a vast investigation on the kinetic study of epoxy resins [17–22] and nanoclay modified epoxy resins [23–26], detail study on the kinetic behavior of CO_2 fixation/nanoclay modified epoxy resins has not yet been reported in the literature. This study tries to focus on the calculation of the cure kinetic parameters of both unmodified and modified bifunctional epoxy resin. The epoxy resin reacted with carbon dioxide to produce a CO_2 fixation modified epoxy resins. Both the unmodified epoxy resin and CO_2 fixation modified epoxy resin were treated using a nanoclay additive. The cure kinetic parameters of the resins were calculated based on Sbirrazzuoli approach that is able to obtain kinetic parameters rather than modeling values.

2. Kinetic analysis

In studying the cure kinetic behavior of thermoset resins such as epoxies, two basically different methods, model fitting [21,27,28] and model-free [29–32] methods, are used. In model fitting method, a well known model, such as Kamal model, is suggested and its kinetic parameters are determined using linear or

* Corresponding author.
E-mail address: m.vafayan@ippi.ac.ir (M. Vafayan).

http://dx.doi.org/10.1016/j.tca.2015.08.024
0040-6031/© 2015 Elsevier B.V. All rights reserved.

non-linear curve-fitting techniques. The activation energy and pre-exponential factor obtained from model fitting techniques cannot be expressed as a function of extent of conversion, i.e. they are apparent values. In fact, the kinetic parameters calculated from model fitting method are modeling values not necessary real kinetic parameters [33].

In contrast to model fitting method, in model free methods, kinetic parameters are estimated without needing a kinetic model. Indeed, in these methods, the activation energy is calculated based on the isoconversional principle in a model-free way.

The rate of a single-step reaction can be expressed as a function of the temperature, T, and the extent of conversion, α, as follows:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where $k(T)$ is the rate constant, $f(\alpha)$ is the reaction model and t is the time. An Arrhenius-type equation is commonly used to describe the relationship between the rate constant and temperature:

$$k(T) = A\exp\left(-\frac{E}{RT}\right) \tag{2}$$

where A and E are, respectively, the pre-exponential factor and the activation energy for a single-step reaction and R is the universal gas constant.

The fundamental assumption of the isoconversional methods is that the reaction model $f(\alpha)$, as defined in Eq. (1), is constant (do not depend on the temperature or heating rate) for a constant value of the extent of conversion. Therefore, the reaction rate, $d\alpha/dt$, at a given extent of conversion is only a function of temperature so that [34]:

$$\left[\frac{\partial \ln(d\alpha/dt)}{\partial T^{-1}}\right]_{\alpha} = -\frac{E_\alpha}{R} \tag{3}$$

where the subscript α indicates isoconversional values.

A large number of isoconversional computational methods are presented by various researchers [32,35,36]. For avoiding problems and inaccuracies associated with most isoconversional computational methods, an advanced nonlinear integral isoconversional method has been proposed by Vyazovkin [37,38] which also adopted in our work. According to this method for a set of n experiments carried out at different arbitrary heating programs $T_i(t)$, the activation energy is determined at any particular value of α by fitting the value of E_α that minimizes the function Φ defined as follows [30]:

$$\Phi(E_\alpha) = \sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{J[E_\alpha, T_i(t_\alpha)]}{J[E_\alpha, T_j(t_\alpha)]} \tag{4}$$

in Eq. (4) the integral

$$J[E_\alpha, T_i(t_\alpha)] = \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} \exp\left(\frac{-E_\alpha}{RT_i(t)}\right) dt \tag{5}$$

is evaluated numerically, using the trapezoidal rule, for a set of experimental heating programs. A computer code was developed based on genetic algorithm to minimize $\Phi(E_\alpha)$, as defined in Eq. (4), for α values between 0.01 and 0.99 with a step of $\Delta\alpha = 0.01$.

The value of A at any given extent of conversion, A_α, can be evaluated using compensation effect [39,40] that is typically found in the following form:

$$\ln A_\alpha = aE_\alpha + b \tag{6}$$

where a and b are constants. In accordance with Eq. (6), only one value of $\ln A$ corresponds to each E value.

Sbirrazzuoli [33] proposed a new approach to compute the kinetic parameters of a given model, such as Kamal's model, using the dependency of E_α on α (or on T) obtained from advanced integral isoconversional method. In this method, the isoconversional principle, Eq. (3), is applied to the Kamal model:

$$\frac{d\alpha}{dt} = [k_1(T) + k_2(T)\alpha^m](1-\alpha)^n \tag{7}$$

to obtain the following equation [34,42]:

$$E_\alpha \equiv E_\alpha(T) = \frac{(A_1/A_2)\exp(-E_1/RT)E_1 + \exp(-E_2/RT)E_2\alpha^m}{(A_1/A_2)\exp(-E_1/RT) + \exp(-E_2/RT)\alpha^m} \tag{8}$$

where $k_1 = A_1\exp(-E_1/RT)$ and $k_2 = A_2\exp(-E_2/RT)$. The kinetic parameters A_1/A_2, E_1, E_2 and m can be computed using Eq. (8), E_α-dependency, instead of Eq. (7), rate-dependency. Under this condition, the obtained kinetic parameters have physical meaning and are not merely modeling values.

Eq. (8) can be applied only on the chemically controlled region of curing reaction. As the curing reactions are going on and the resin becomes crosslinked, molecular motions become more restricted and the rate-controlling step of curing shifts from the chemically reaction to diffusion.

In a mixed diffusion-kinetic regime, the effective activation energy E_{ef} is a function of the activation energies of both chemical reaction (E) and diffusion (E_D) [41]:

$$E_{ef} = \frac{k(T)E_D + k_D(T,\alpha)E}{k(T) + k_D(T,\alpha)} \tag{9}$$

Where $k(T)$ and $K_D(T,\alpha)$ are the reaction and diffusion rate constants. Introducing $k(T) = A\exp(-E/RT)$ and $K_D(T,\alpha) = D_o\exp(-E_D/RT + K\alpha)$ into Eq. (9) [33,41]:

$$E_\alpha \equiv E_\alpha(T) = \frac{(A/D_o)\exp(-E/RT)E_D + \exp(-E_D/RT + K\alpha)E}{(A/D_o)\exp(-E/RT) + \exp(-E_D/RT + K\alpha)} \tag{10}$$

where K is a constant accounting for the effect of the chemical reaction on the change in diffusivity, D_o is the pre-exponential factor and E_D is the activation energy of diffusion. The kinetic parameters A/D_o, E, E_D and K can be computed using Eq. (10).

3. Experimental

3.1. Materials

Chemical structures of used materials including technical-grade epoxy, curing agent, catalyst and reactive diluent are shown in Table 1. A commercial grade epoxy resin mainly based on diglycidyl ether bisphenol A (DGEBA) with 185–192 EEW was cured with diethylenetriamine in the presence of tetra-*n*-butyl ammonium bromide as catalyst. Organo-montmorillonite (Cloisite 30B) from Southern Clay Products was used as nanoclay. Reactive diluent (3,4 epoxy cyclo hexyl methyl-3,4 epoxy-cyclo hexane carboxylate) (ECC) was used to reduce the viscosity of the system. Methyl ethyl ketone (MEK) was used as solvent provided by DAE Jung.

3.2. Preparation of CO_2 fixation modified epoxy resin (CFME)

65 g of the epoxy resin, 3 g TBAB and 65 g MEK were poured into a flask and mixed at 78 °C for 1 h, and then CO_2 was purged into the mixture. CO_2 fixation reaction was conducted and 39% cyclic carbonate (39% CFME) was formed after 225 min. Then 39 g reactive diluent was added to the 39% CFME.

Download English Version:

https://daneshyari.com/en/article/7062314

Download Persian Version:

https://daneshyari.com/article/7062314

Daneshyari.com